JOURNAL OF SOLID STATE CHEMISTRY **43**, 339–345 (1982)

The Crystal Structure of β-Ga_2Se_3

D. LÜBBERS AND V. LEUTE

Institut für Physikalische Chemie
der Universität Münster, Schlossplatz 4, D-4400 Münster, Germany

Received December 21, 1981

From new X-ray powder diffraction data reported in this paper, the structure of the ordered, superstructural phase of Ga_2Se_3 is found to be different from the structures stated in the literature up to now. The difference relates essentially to the structure distortion involved in the formation of the superstructure. This distortion is clarified in a way which, in general, is suitable for investigations of small distortions of cubic structures. The superstructure cell turns out to be monoclinic, with $a = 6.6608(3)$, $b = 11.6516(4)$, $c = 6.6491(3)$ Å, $\beta = 108.840(5)°$, and $Z = 4$. Furthermore, the coordinates of the Ga and Se positions in this cell are deduced. The space group is shown to be C_s^4-Cc (No. 9).

Introduction

The structure of β-Ga_2Se_3 is a superstructure, originating from the zinc blende-type structure of α-Ga_2Se_3 (*1*), in which one-third of the cation sites are vacant. The formation of the superstructure results from the ordering of the randomly distributed Ga atoms and "structural vacancies" on the cation sites of the zinc blende lattice. In the literature, we find three different structures proposed for β-Ga_2Se_3 by different authors (*2–4*). These three structures differ in the superstructure unit cell and space group, whereas the underlying substructure is the same in all the three cases, namely, tetragonal, with lattice constants close to the constant of α-Ga_2Se_3.

The lines we observed in our X-ray powder films and diffractometer diagrams made us doubt whether any of the three structures was correct. That given by Ghémard *et al.* (*3*) does not allow all the lines we found. Furthermore, there are some greater differences between the angles of the expected and the observed reflections. Palatnik and Belova (*2*) suggest a structure allowing many additional reflections. But we could not find these additional lines. Finally, the structure proposed by Khan and Ali (*4*) demands a number of reflections which is much too great compared to the number of observed lines. Thus we attempted a new analysis of the β-Ga_2Se_2 structure.

Experimental

We prepared our Ga_2Se_3 by fusion of the very pure elements (Ga, 99.9999%, Se, 99.999%, from Koch-Light Laboratories, England) in sealed evacuated quartz ampoules. We found that the best method for obtaining the β phase is to apply an excess of Se and to quench the compound directly after its crystallization from the melt, with subsequent annealing between 550 and 600°C for a few weeks. By applying 39.5 mole% Ga and 60.5 mole% Se, Se saturation of the β-Ga_2Se_3 is achieved because,

0022-4596/82/090339-07$02.00/0

after the annealing, Se in elemental form is still found besides the compound. This was clarified by electron microprobe measurements. After being quenched from its liquid phase, the Se was noncrystalline and did not disturb the X-ray diffraction measurements. The β-Ga_2Se_3 crystals have a brown color, they are brittle, and can be powdered easily.

The X-ray diffraction was measured with a diffractometer (Cu$K\alpha$ radiation) and a Guinier camera (Cu$K\alpha_1$). Adjusting the apparatus, we concentrated our efforts on achieving maximum resolution. The $K\alpha_1$ and $K\alpha_2$ components in the diffractometer diagrams were resolved for $\Theta > 13°$. We preferred the diffractometer diagrams to the Guinier films because of the higher resolution and precision. If Cu$K\beta$ reflections were disturbing, we made use of the films. Numerical values used were $\lambda(K\alpha_1) = 1.54051$, $\lambda(K\alpha) = 1.54178$ Å.

Powder Diffraction Data

The interplanar spacings, d_{obs}, and the relative intensities, I_{obs}, calculated from the measured reflections are given in Table I. The estimated maximum error of the intensities is ± 20% ± 1, taking account of the statistic variations and the difficulty in resolving superposed lines. In some Θ regions there are very closely bunched lines. Their analysis is complicated by the superposition of the $K\alpha_1$ and $K\alpha_2$ components. The relative intensities of the lines differ quite a lot between diagrams originating from different preparations. This allows one, in some cases, to resolve the superposed lines by the combined evaluation of several diagrams.

The data show that the intense lines appear in groups. Each of these groups is placed in a region, where the α phase would display a line. The weaker lines are more uniformly distributed and also appear at lower angles. The two types of lines do not differ in line sharpness.

We assume that the weaker, more uniformly distributed lines originate from the superstructure only, whereas the groups of intense lines are generated by the substructure, which is similar to the structure of the α phase and emerges from this by a small distortion associated with the formation of the superstructure. The symmetry decrease, caused by the distortion, results in a splitting of the single α-phase lines.

Our observation of the similar sharpnesses of the superstructure and substructure lines makes us assume that the distortion is nearly homogeneous; i.e., the cation and the anion lattices are distorted equally, and the substructure cells are distinguishable only by the different arrangements of the Ga atoms on the cation sites. Apart from that, the periodicity of the substructure is preserved. One can imagine this homogeneous distortion as a distortion of a homogeneous, elastic substance into which the atom sites are embedded. Nevertheless, small deviations from the homogeneity of the distortion are to be expected around the structural vacancies.

Method of Analysis

In order to determine the symmetry of the substructure, we consider the number of lines into which one cubic reflection line splits, if the cubic lattice is distorted into a triclinic one. This number of different triclinic lines depends on the type of the original cubic reflection, i.e., on its Miller indices, how many of them are equal, and how many are zero. Then we consider how many of these different triclinic lines remain different and how many coincide in the case of any distortion leading to a symmetry higher than the triclinic one. The results of these considerations are compiled in Table II. For the triclinic and the monoclinic sys-

TABLE I

X-RAY POWDER DIFFRACTION DATA OF β-Ga_2Se_3

No.[b]	h k l	d_{calc}/Å	d_{obs}/Å	I_{obs}
1	0 2 0	5.8258	5.829	2
2	1 1 0	5.5445	5.554	4
3	1 1 $\bar{1}$	4.9087	4.914	<1
4	0 2 1	4.2751	4.278	3
5	1 1 1	3.6745	3.679	1
7[a]	1 3 $\bar{1}$	3.1555	3.1551	100
8[a]	2 0 0	3.1520	3.1530	50
9	1 1 $\bar{2}$	3.1469	3.1474	50
10[a]	0 0 2	3.1464		
11	0 4 0	2.9129	2.9125	2
12	2 2 $\bar{1}$	2.8535	2.8544	3
13	2 2 0	2.7722	2.7742	2
14	0 2 2	2.7685	2.7692	3
15[a]	1 3 1	2.7421	2.7420	5
16[a]	2 0 $\bar{2}$	2.7062	2.7072	3
17	0 4 1	2.6434	2.6443	2
19	2 2 $\bar{2}$	2.4543	2.4544	7
20	1 1 2	2.4537		
21	2 2 1	2.3067	2.3066	3
22	1 5 0	2.1858	2.1861	3
23	3 1 $\bar{1}$	2.1809	2.1801	<1
24	1 1 $\bar{3}$	2.1772	2.1770	<1
25	2 4 $\bar{1}$	2.1760	2.1750	<1
26	1 5 $\bar{1}$	2.1404	2.1406	<1
27	2 4 0	2.1393		
28	0 4 2	2.1375		
30	3 1 0	2.0680	2.0682	1
31	3 1 $\bar{2}$	2.0534	2.0531	2
32	1 5 1	1.9966	1.9960	<1
33	2 4 $\bar{2}$	1.9826	1.9819	<1
34	0 2 3	1.9736	1.9738	<1
35	2 2 $\bar{3}$	1.9623	1.9620	1
36[a]	0 6 0	1.9419	1.9417	20
37[a]	2 0 2	1.9361	1.9363	20
38[a]	3 3 $\bar{1}$	1.9274	1.9269	40
39[a]	1 3 $\bar{3}$	1.9249	1.9247	40
40	2 4 1	1.9024	1.9023	2
41	1 5 $\bar{2}$	1.8974	1.8982	<1
42	0 6 1	1.8556	1.8553	<1
44	3 3 $\bar{2}$	1.8377	1.8388	<1
45	2 2 2	1.8373	1.8370	<1
46	3 1 1	1.8021	1.8010	<1
47	1 1 3	1.8000		
48	3 1 $\bar{3}$	1.7829	1.7831	1
49	1 5 2	1.7078	1.7079	1
51	2 4 $\bar{3}$	1.6949	1.6952	<1
52	2 6 $\bar{1}$	1.6701	1.6698	<1
53[a]	2 6 0	1.6533	1.6535	7
54[a]	0 6 2	1.6525	1.6524	7
55[a]	3 3 1	1.6510	1.6505	7
56[a]	1 3 3	1.6494	1.6491	7
58[a]	4 0 $\bar{2}$	1.6365	1.6361	10
59[a]	3 3 $\bar{3}$	1.6362		
60[a]	2 0 $\bar{4}$	1.6342	1.6337	3
67[a]	2 6 $\bar{2}$	1.5778	1.5776	1
70	2 2 $\bar{4}$	1.5735	1.5734	1
71[a]	0 0 4	1.5732		
73	3 5 $\bar{2}$	1.5543	1.5539	1
77	4 2 0	1.5213	1.5208	<1
78	3 1 2	1.5205		
79	0 2 4	1.5188	1.5190	<1
81	1 7 $\bar{2}$	1.4832	1.4833	<1
88	4 4 $\bar{2}$	1.4268	1.4265	<1
89	3 5 $\bar{3}$	1.4266		
90	3 3 2	1.4264		
101[a]	2 6 2	1.3711	1.3710	6
103[a]	4 0 $\bar{4}$	1.3531	1.3530	4
105	4 4 $\bar{3}$	1.3455	1.3453	<1
108	1 7 $\bar{3}$	1.3309	1.3307	<1
109	2 8 $\bar{1}$	1.3307		
112	5 1 $\bar{2}$	1.3191	1.3190	<1
115	1 1 $\bar{5}$	1.3103	1.3104	<1
116	3 7 0	1.3048	1.3045	<1
117	3 7 $\bar{2}$	1.3011	1.3012	1
120	2 8 $\bar{2}$	1.2825	1.2823	<1
123	3 5 $\bar{4}$	1.2707	1.2706	1
124	5 1 $\bar{3}$	1.2705		
125	3 1 $\bar{5}$	1.2690	1.2689	<1
128	2 8 1	1.2600	1.2601	<1
129[a]	1 9 $\bar{1}$	1.2591	1.2591	3
131[a]	4 0 2	1.2560	1.2558	3
132[a]	2 0 4	1.2550	1.2549	3
133	5 1 0	1.2535	1.2536	<1
134[a]	4 6 $\bar{2}$	1.2514	1.2517	2
135[a]	5 3 $\bar{1}$	1.2507	1.2507	4
136[a]	2 6 $\bar{4}$	1.2504	1.2500	4
137[a]	1 3 $\bar{5}$	1.2487	1.2486	4
138	0 2 5	1.2302	1.2301	<1
141	4 2 2	1.2278	1.2277	<1
142[a]	1 9 1	1.2278		
145[a]	3 3 3	1.2248	1.2247	<1
146[a]	4 6 0	1.2237	1.2232	<1
147	3 7 $\bar{3}$	1.2234		
148[a]	0 6 4	1.2224		
149[a]	5 3 $\bar{3}$	1.2141	1.2143	1
150	1 5 4	1.2140		
151[a]	3 3 $\bar{5}$	1.2128	1.2127	<1
158	2 8 $\bar{3}$	1.1938	1.1938	<1
161	0 10 0	1.1652	1.1652	<1
167	5 5 $\bar{2}$	1.1536	1.1537	<1
173	1 5 $\bar{5}$	1.1477	1.1477	<1
174	0 10 1	1.1457	1.1456	1
180	3 5 $\bar{5}$	1.1196	1.1196	1
181[a]	3 9 $\bar{1}$	1.1184	1.1183	3
182[a]	1 9 $\bar{3}$	1.1179	1.1180	3
183[a]	5 3 1	1.1166	1.1165	4
184[a]	1 3 5	1.1151	1.1152	4
185[a]	4 6 $\bar{4}$	1.1102	1.1102	6
186[a]	6 0 $\bar{2}$	1.1101		
188[a]	2 0 $\bar{6}$	1.1081	1.1081	2
193	3 1 4	1.0955	1.0954	1
194	4 8 $\bar{1}$	1.0949	1.0950	1
195	2 6 $\bar{5}$	1.0948		
204	4 2 3	1.0817	1.0818	<1
216	2 8 3	1.0558	1.0559	2
217[a]	3 9 1	1.0557		
219[a]	4 6 2	1.0546	1.0544	1
220[a]	2 6 4	1.0540		
223[a]	3 9 $\bar{3}$	1.0518	1.0518	<1
226	3 3 $\bar{6}$	1.0490	1.0491	<1
227[a]	0 0 6	1.0488		
229[a]	6 0 $\bar{4}$	1.0430	1.0428	2
230[a]	5 3 $\bar{5}$	1.0428		
231	5 5 1	1.0426		
232[a]	4 0 $\bar{6}$	1.0420	1.0419	1
246	6 4 $\bar{1}$	1.0253	1.0253	<1
260	2 10 2	0.9983	0.9984	<1
279[a]	4 0 4	0.9680	0.9682	<1
284[a]	2 6 $\bar{6}$	0.9625	0.9626	<1

[a] Reflection originating from the substructure.

[b] Number refers to the set of calculated reflections; the absence of a number indicates that the reflection was not found experimentally.

tems, additional special symmetries are considered because more lines coincide in these special cases than in the general triclinic and monoclinic symmetries, respectively. The hexagonal system is not listed because its unit cell cannot be produced out of the cubic one by only a small distortion. Now, Table II can be used to find the crystal system of a distorted cubic lattice from the observed splitting of some of the cubic lines. In the following, we will make use of this method.

From Table I, we extract four groups of substructure lines by their comparatively high intensities. We name each group after the indices of the corresponding α-Ga_2Se_3 reflection found in the same region of angle. The four groups are: the 111 group with d_{obs}/Å = 3.1551 (s), 3.1530, 3.1474; the 220 group with d_{obs}/Å = 1.9417, 1.9363, 1.9269

TABLE II

MULTIPLICITY OF LINE SPLITTING BY A SMALL DISTORTION OF A CUBIC LATTICE

Symmetry of distorted unit cell	Reflection indices					
	Two indices 0	One index 0, the others with equal abs. values	One index 0, the others with differ. abs. values	No index 0, all indices with equal abs. values	No index 0, two indices with equal abs. values	No index 0, all indices with differ. abs. values
Triclinic	3 * 1	6 * 1	12 * 1	4 * 1	12 * 1	24 * 1
Triclinic, special $a_0 = b_0, \alpha_0 = \beta_0$	1 * 2 + 1 * 1	2 * 2 + 2 * 1	6 * 2	1 * 2 + 2 * 1	5 * 2 + 2 * 1	12 * 2
Monoclinic	3 * 1	2 * 2 + 2 * 1	4 * 2 + 4 * 1	2 * 2	6 * 2	12 * 2
Monoclinic, special $a_0 = c_0, \beta_0 \neq 90°$	1 * 2 + 1 * 1	1 * 4 + 2 * 1	2 * 4 + 2 * 2	2 * 2	2 * 4 + 2 * 2	6 * 4
Orthorhombic	3 * 1	3 * 2	6 * 2	1 * 4	3 * 4	6 * 4
Rhombohedral	1 * 3	2 * 3	2 * 6	1 * 3 + 1 * 1	1 * 6 + 2 * 3	4 * 6
Tetragonal	1 * 2 + 1 * 1	1 * 4 + 1 * 2	3 * 4	1 * 4	1 * 8 + 1 * 4	3 * 8
Cubic	1 * 3	1 * 6	1 * 12	1 * 4	1 * 12	1 * 24

Note. $m * n$ means m different lines, each one composed of n coinciding triclinic lines.

(s), 1.9247 (s); the 311 group with $d_{obs}/\text{Å}$ = 1.6535, 1.6524, 1.6505, 1.6491, 1.6361 (s), 1.6337 (w); the 400 group with $d_{obs}/\text{Å}$ = 1.3710 (s), 1.3530. The lines labeled (s) are stronger, and those labeled (w) are weaker than the other lines of the same group. Now, making use of Table II, we can conclude from these groups that the substructure must be the special triclinic one, with $a_0 = b_0$ and $\alpha_0 = \beta_0$. (The 1.6361-Å line of the 311 group is assumed to contain unresolved the second weaker reflection.) Thus the tetragonal substructure, suggested in the literature, must be replaced by a triclinic one.

Lattice Parameters

We propose a superstructure unit cell with the same content of formula units (4 Ga_2Se_3) and with similar volume and shape as that stated by Ghémard *et al.* It can be regarded as being composed of two quarters of the unit cell first suggested by Palatnik and Belova. The symmetry, however, of our unit cell must be another one, being compatible with the triclinic symmetry of the substructure. Figure 1 shows the triclinic substructure cell and the superstructure cell, each of them embedded into the lattice of an alternative substructure, the cell of which is body centered and has half the volume of the triclinic cell. The relations between the different cells can be taken from Fig. 1. Therefore, both the smaller substructure cell and the superstructure cell must be monoclinic with all the three edges having different lengths.

According to this superstructure unit cell, all the lines observed can be indexed (see Table I). Least-squares analysis of all the observed reflections yields the following values for the superstructure lattice parameters (with the standard deviations in parentheses): $a = 6.6608(3)$, $b = 11.6516(4)$, $c = 6.6491(3)$ Å, $\beta = 108.840(5)°$. From these values, the lattice parameters for the triclinic and the monoclinic substructures are calculated—face-centered triclinic: $a_0 = b_0 = 5.4843(3)$, $c_0 = 5.4125(3)$ Å, $\alpha_0 = \beta_0 = 90.075(4)°$, $\gamma_0 = 90.174(5)°$; body-centered monoclinic: $a_m = 3.8721(2)$, $b_m = 3.8839(2)$, $c_m = 5.4125(3)$ Å, $\beta_m = 90.106(6)°$. The volume of the superstructure cell is $V = 3 \cdot V_0 = 6 \cdot V_m = 488.39(3)$ Å^3, and the resulting X-ray density is $d_X = 5.118$ g/cm^3. The calculated angles of the reflections are in convincingly good agree-

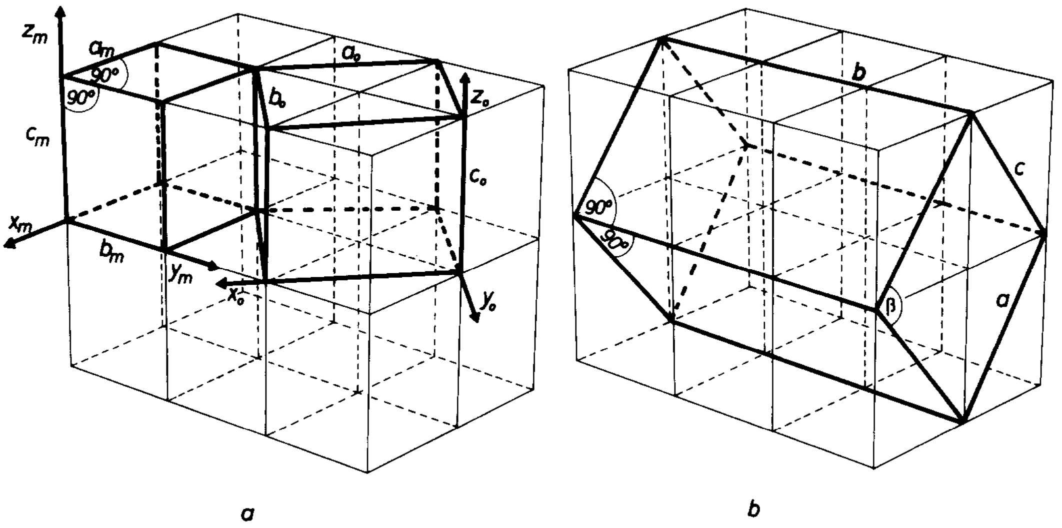

FIG. 1. Relations between the two different substructure cells (a) and the superstructure cell (b). The indices 0 and m refer to the face-centered triclinic and the body-centered monoclinic substructures, respectively.

ment with the observed ones. The figure of merit after de Wolff (*5*), a reliability criterion, is $M_{20} = 58$.

Position Coordinates and Space Group

The conditions limiting possible reflections are found to be $h + k = 2 \cdot n$ and, with $k = 0$, $l = 2 \cdot n$. The only monoclinic space groups fulfilling these conditions are C_s^4-Cc and C_{2h}^6-$C2/c$, Nos. 9 and 15, respectively, of the International Tables for X-Ray Crystallography (*6*).

A consequence of a strictly homogeneous distortion is that the coordinates of the atom positions in the distorted and in the undistorted lattice are exactly the same. Therefore, with the assumption of homogeneous distortion, the atom positions in the superstructure cell can be calculated. Now, we must find out which of the cation sites have to be vacant according to the order of the superstructure. If we take the corners of the superstructure cell as occupied by structural vacancies (SV), the centers of the C faces must also be occupied by SV because of the reflection condition $h + k = 2 \cdot n$. Thus two of the four vacant cation sites per unit cell are already fixed. The other two are given by the second reflection condition, saying that there is a (010) glide plane with a $c/2$ translation in [001] direction. The spacing between this glide plane and the B face can only be $[(2 \cdot n + 1)/12]\ b$. From these values, $\frac{3}{12} \cdot b$ and $\frac{9}{12} \cdot b$ are ruled out because they are consistent only with an all-faces centered unit cell. Figure 2 shows the arrangement of the Ga atoms and SV on the cation sites. This arrangement results from each of the only possible spacings, $\frac{1}{12} \cdot b$, $\frac{5}{12} \cdot b$, $\frac{7}{12} \cdot b$, and $\frac{11}{12} \cdot b$.

Figure 2 also shows the Se positions. According to Newman (*7*), the Se atoms are called Se(X) (Se(Y)), when their nearest neighbors are two Ga and two SV (three Ga and one SV). One-third of the anion sites are occupied by Se(X) and two-thirds by Se(Y).

After a $\frac{1}{12} \cdot b$ translation of the coordinate system in [010] direction, the new coordinates x, y, z of the SV, Ga, Se(X), and Se(Y) positions are the following. SV: 0, $\frac{11}{12}$,

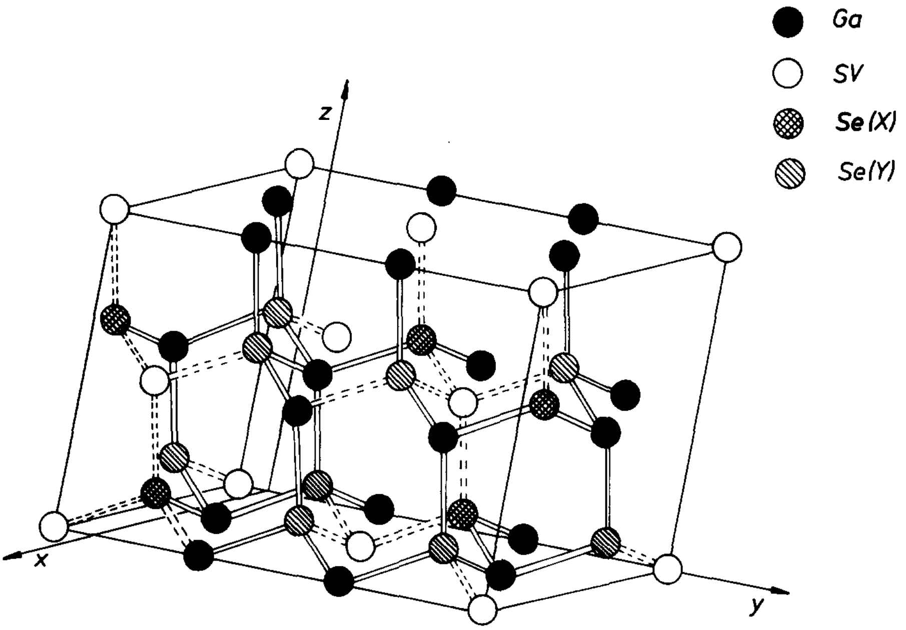

FIG. 2. Positions in the superstructure unit cell. Se(X) is neighbored by two, Se(Y) by three, Ga atoms.

0; Ga: 0, $\frac{7}{12}$, 0 and 0, $\frac{3}{12}$, 0; Se(X): $\frac{3}{8}$, $\frac{7}{12}$, $\frac{1}{8}$; Se(Y): $\frac{3}{8}$, $\frac{3}{12}$, $\frac{1}{8}$ and $\frac{3}{8}$, $\frac{11}{12}$, $\frac{1}{8}$; plus the coordinates of the equivalent positions for the space group C_s^4-Cc according to the International Tables. Thus this space group is just the right one. The additional symmetry elements of the space group C_{2h}^6-$C2/c$ would be correct only if SV, Ga, Se(X), and Se(Y) were equivalent.

Additional Remarks

The type of structure distortion associated with the ordering of the Ga atoms on the cation sites can be predicted. For this purpose, it is sufficient to check which of the {100} and which of the {111} sets of the planes of the *fcc* phase with random Ga distribution become inequivalent by the Ga ordering. Inequivalence can be assumed to result in different spacings. As the Ga arrangements on the (100) and the (010) plane sets are also the same after ordering, whereas on the (001) plane set Ga is ordered in a different manner, one can predict $a_0 = b_0 \neq c_0$ and $\alpha_0 = \beta_0 \neq \gamma_0$. Of the plane sets (111), (11$\bar{1}$), (1$\bar{1}$1), and ($\bar{1}$11), only the two latter ones show equivalent Ga arrangements after the ordering. The inequivalence of the two former ones results in $a \neq c$ or $\beta_m \neq 90°$ or $\alpha_0 \neq 90°$. The inquivalence of the first and the third one makes $a_m \neq b_m$ or $\gamma_0 \neq 90°$.

The superstructural ordering of Ga leaves unchanged the fact that, on the average of the whole crystal, each of the four cation sites in the face-centered substructure cell is occupied by Ga with the same frequency, which is two-thirds. This is in agreement with the reflection conditions found.

Our results confirm some general statements made by Newman (*7*, *8*) about the ordering in $A_2^{\mathrm{III}}B_3^{\mathrm{VI}}$ compounds having tetrahedral bonding. For instance, in our β-Ga_2Se_3 structure, the nearest neighbors of any Ga atom really are one Se(X) and three Se(Y), and any SV really neighbors two

Se(*X*) and two Se(*Y*). The next nearest neighbors also agree with Newman's predictions. Moreover, the SV and the Se(*X*) form continuous, unbranched chains through the crystal; these chains are [001] directed. The (001) planes of the β-Ga_2Se_3 superstructure are a realization of the hexagonal nets specified by Newman. They build up the β-Ga_2Se_3 structure by stacking in the sequence –V–III–V–III– according to Newman's nomenclature.

Newman (*8*) states the structure of the ordered phase of the sulfide Ga_2S_3 to be built up from the hexagonal nets by –II–VI–II–VI– stacking and to have the space group C_s^4-*Cc*. Comparison with the β-Ga_2Se_3 phase shows that different stacking of equal planes results in the same superstructure, but different substructures of the wurtzite type and the zinc blende type, respectively. The C faces of the two superstructure cells correspond completely, whereas the monoclinic angle of the Ga_2S_3 cell is made with the longer side of the C face instead of with the shorter one. Each of the two unit cells contains four formula units. The structure of the unordered Ga_2S_3 phase also undergoes a small distortion associated with the ordering (*9*). So, there is a close relation between Ga_2S_3 and Ga_2Se_3 not only for the unordered but also for the ordered phases.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is acknowledged.

References

1. H. Hahn and W. Klingler, *Z. Anorg. Allg. Chem.* **259**, 135 (1949).
2. L. S. Palatnik and E. K. Belova, *Inorg. Mater.* **1**, 1703 (1965).
3. G. Ghémard, R. Ollitrault-Fichet, and J. Flahaut, *C.R. Acad. Sci. Paris Ser. C* **282**, 831 (1976).
4. M. Y. Khan and S. Z. Ali, *J. Appl. Crystallogr.* **10**, 70 (1977).
5. P. M. de Wolff, *J. Appl. Crystallogr.* **1**, 108 (1968).
6. "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham (1952).
7. P. C. Newman, *J. Phys. Chem. Solids* **23**, 19 (1962).
8. P. C. Newman, *J. Phys. Chem. Solids* **24**, 45 (1963).
9. J. Goodyear and G. A. Steigmann, *Acta Crystallogr.* **16**, 946 (1963).